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SUPPORTING INFORMATION

Title: Gold Catalysis: Evidence for the In-situ Reduction of Gold(III) During the Cyclization of Allenyl Carbinols
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Synthesis of 1

Under dinitrogen 1-ethynyl-1-cyclohexanol (11.2 g, 90.2 mmol), para-formaldehyd (6.70 g, equivalent to 223 mmol of formaldehyde) and diisopropylamine (23.5 ml, 167 mmol) were dissolved in dioxane (140 ml). Copper(I)-bromide (6.56 g, 45.7 mmol) was added and the suspension was refluxed for 3 h. After filtration (celite) the volume was reduced in vacuo, diethyl ether (100 ml) was added and the solution was washed with brine. The organic layer was dried over $MgSO_4$, the solvent was removed and the crude product was purified by column chromatographly on silica gel (hexane/ethyl acetate, 10:1). 4.80 g (38%) of the known[1] **1** were isolated. R_f (hexane/ethyl acetate, 10:1) = 0.18; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 5.29 (t, J = 6.7 Hz, 1H), 4.88 (d, J = 6.6 Hz, 2H), 1.70-1.30 (m, 10H).

Synthesis of 5

Under dinitrogen 1,1-diphenyl-2-propin-1-ol (5.00 g, 24.0 mmol), para-formaldehyde (5.00 g, equivalent to 167 mmol of formaldehyde), diisopropylamine (5.43 ml, 38.6 mmol), copper(I)-bromide (1.73 g, 12.1 mmol) were dissolve in THF (45 ml). After refluxing for 8 h, the suspension was filtered (celite), diethyl ether (100 ml) was added and the solution was washed with brine. The organic layer was dried over $MgSO_4$, the solvent was removed and the crude product was purified by column chromatography on silica gel (hexane/ethyl acetate, 20:1). 799 mg (15%) of the known[2] **5** were isolated, the major product was the undesired and known 4-diisopropylamino-1,1-diphenyl-but-2-yn-1-ol (**11**)[3] (3.35 g, 43%). **5**: R_f (hexane/ethyl acetate 10:1) = 0.26; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.46-7.22 (m, 10H), 5.96 (t, J = 6.5 Hz, 1H), 4.99 (d, J = 6.5 Hz, 2H), 2.61 (s, 1H). **11**: R_f (hexane/ethyl acetate 10:1) = 0.16; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.61-7.58 (m, 4H), 7.35-7.21 (m, 6H), 3.60 (s, 2H), 3.20 (sept, J = 6.5 Hz, 2H), 2.75 (s, 1H), 1.10 (d, J = 6.6 Hz, 12H); ^{13}C NMR (62.9 MHz,

$CDCl_3$): δ = 145.4 (s, 2C), 128.2 (d, 4C), 127.6 (d, 2C), 126.1 (d, 4C), 87.1 (s), 86.0 (s), 74.6 (s), 48.5 (d, 2C), 34.4 (t, 2C), 20.8 (q, 4C).

Reaction of 5 with $AuCl_3$

Under an atmosphere of dinitrogen to **5** (500 mg, 2.25 mmol) in acetonitrile (6 ml) $AuCl_3$ (33.9 mg, 112 μmol) was added at room temperature. The reaction was monitored by tlc, after consumption of the starting material the solvent was removed and the crude material was purified by column chromatography on silica gel (hexane/ethyl acetate, 20:1). Thus 154 mg (31%) of known **6**,[4] 30.7 mg (6%) of the hitherto unknown **7**, 43.8 mg (8%) of known **8**,[5] 19.1 mg (4%) of known **9**[6] and 102 mg (21%) of the hitherto unknown **10** were obtained. **6**: R_f (hexane/ethyl acetate, 10:1) = 0.47; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.36-7.23 (m, 10H), 6.31 (dt, *J* = 6.1 Hz, 2.4 Hz, 1H), 6.05 (dt, *J* = 6.1 Hz, 1.6 Hz, 1H), 4.85 (dd, *J* = 2.4 Hz, 1.6 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 145.1 (s), 132.4 (d), 128.0 (d), 127.0 (d), 126.2 (d), 74.9 (t). **7**: M. p.: 114 °C; R_f (hexane/ethyl acetate, 10:1): 0.22; IR (neat): nu(tilde) = 3448, 2925, 1718, 1447, 1059, 699 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.56-7.09 (m, 20H), 6.19 (t, *J* = 1.8 Hz, 1H), 5.03 (d, *J* = 1.8 Hz, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 144.9 (s, 2C), 132.0 (d, 2C), 130.3 (s, 2C), 128.6 (d, 8C), 127.8 (d, 4C), 126.7 (d, 8C), 77.6 (t, 2C); C, H analysis calcd. (%) for $C_{32}H_{26}O_2$ (442.6): C 86.85 H 5.92; found: C 86.67 H 5.79. **8**: M.p.: 37 °C; R_f (hexane/ethyl acetate, 10:1): 0.56; IR (neat): nu(tilde) = 3590, 1700, 1684, 1654, 1597, 1491, 1447, 1075, 1032, 765, 697 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.41-7.22 (m, 10H), 6.46 (d, *J* = 1.1 Hz, 1H), 5.24 (d, *J* = 1.3 Hz, 1H), 4.99 (t, *J* = 1.2 Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 145.4 (s), 141.5 (s), 139.0 (s),136.8 (s), 129.7 (d, 2C), 128.14 (d, 2C), 128.10 (d, 3C), 127.7 (d, 2C), 127.6 (d),125.0 (d), 116.7 (t); MS (70 eV): *m/z* (%)**:** 240 (23) [M^+], 18 (67), 203 (30), 205 (100). **9**: R_f (hexane/ethyl acetate, 10:1): 0.47; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.48-7.28 (m, 10H), 6.02 (d, *J* = 2.6 Hz, 1H), 3.01 (d, *J* =2.6

Hz, 1H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 154.3 (s), 140.9 (s), 138.7 (s), 129.7 (d, 2C), 128.4 (d), 128.1 (d, 3C), 127.80 (d, 2C), 127.77 (d, 2C), 105.8 (d), 82.3 (s), 81.3 (d). **10**: M.p.: 83 °C; R_f (hexane/ethyl acetate, 10:1): 0.36; IR (neat)**:** nu(tilde) = 3421, 1734, 1654, 1598, 1491, 1447, 1277, 1062, 1028, 758, 699 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.32-7.22 (m, 20H), 6.63 (s, 1H), 6.33 (t, *J* = 2.1 Hz, 1H), 4.90 (dd, *J* = 2.1 Hz, 2.7 Hz, 4H); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 145.0 (s), 144.7 (s), 142.7 (s), 139.9 (s), 139.2 (s), 137.5 (s), 132.3 (s), 129.9 (s), 129.7 (d, 2C), 129.1 (d), 128.03 (d, 2C), 128.00 (d, 5C), 127.8 (d, 2C), 127.6 (d), 127.1 (d), 127.0 (d, 2C), 126.23 (d, 4C), 126,21 (d), 125.9 (d), 117.6 (t), 74.3 (t); MS (70 eV): *m/z* (%)**:** 426 (6) [M^+], 18 (35), 105 (100), 337 (18); C, H analysis calcd. (%) for $C_{32}H_{26}O$ (426.6): C 90.11 H 6.14; found: C 90.37 H 5.98.

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